Sustain. Environ. Res., 20(5), 325-331 (2010)
(Formerly, J. Environ. Eng. Manage.)

REMOVAL OF 2,4-DICHLOROPHENOL BY FLUIDIZED-BED FENTON PROCESS

Isara Muangthai,[1] Chavalit Ratanatamsakul[1] and Ming-Chun Lu[2,*]

[1]Department of Environmental Engineering
Chulalongkorn University
Bangkok 10230, Thailand
[2]Department of Environmental Resources Management
Chia Nan University of Pharmacy and Science
Tainan 717, Taiwan

Key Words: Advance oxidation processes, box-Behnken design, fluidized-bed Fenton process, 2,4-dichlorophenol

ABSTRACT

The degradation of 2,4-dichlorophenol (2,4-DCP) by fluidized-bed Fenton process has been optimized by using experimental design methodology. Box-Behnken design was applied to investigate the effects of pH, the amount of carriers, initial H_2O_2 and initial Fe^{2+} concentration on the treatment performance in terms of 2,4-DCP, chemical oxygen demand (COD) and total iron removal efficiencies. Results showed that H_2O_2 concentration had more profound effect than Fe^{2+} in terms of 2,4-DCP removal while, pH and the amount of carriers did not have an obvious effect on 2,4-DCP degradation. Increasing H_2O_2 concentrations could improve COD removal whereas increasing Fe^{2+} concentration more than 0.55 mM would decrease COD removal. The decreased COD performance was probably due to hydroxyl radical scavenging effects. Results also revealed the optimum condition for degrade 2,4-DCP, from the Box-Behnken design prediction: pH 3, 100 g of SiO_2, 0.25 mM of Fe^{2+} and 10 mM of H_2O_2. Under this conditions, 2,4-DCP, COD and total iron removal efficiencies were > 99, 55 and 14%, respectively. Additionally, the total iron removal efficiency at the optimum condition in fluidized-bed Fenton was higher than that in Fenton process. This result demonstrates the advantage of fluidized-bed Fenton process compared with the traditional Fenton technology.

INTRODUCTION

2,4-dichlorophenol (2,4-DCP) is an organic halogen hydrocarbon consisting of phenol and chlorine functional group. It is widely used in numerous industries such as dyes, drugs, pesticides, fungicides, wood preservative, and pharmaceutical manufacturing. 2,4-DCP also has been found in the effluent of disinfected water after chlorination, in the flue gas of municipal waste incineration and in pulp and paper wastewater [1]. It is considered to be hazardous substances and priority toxic pollutants by the U.S. Environmental Protection Agency [2]. This chemical can be toxic to human. It can damage the central nervous system, kidneys, liver, blood-forming organs and it is also suspected to be human carcinogen [3]. However, it is difficult to completely treat wastewater containing 2,4-DCP biologically due to its resistance to biodegradation. Therefore, it requires an alternative treatment method which provides an efficient treatment.

Presently, advanced oxidation processes (AOPs) have been developed for treating a variety of compounds. AOPs are oxidation processes which generate hydroxyl radicals (•OH) in the degradation of toxic organic pollutants [4]. In addition, the Fenton method is more efficient with a lower cost than other AOPs [5]. The Fenton process is based on the electron transfer between ferrous ion and hydrogen peroxide, which acts as a homogenous catalyst, yielding •OH as shown in Eq. 1 that can degrade organic compounds quickly through Eq. 4. Several reactions can take place during the Fenton reaction as shown below [6,7].

$$Fe^{2+} + H_2O_2 \rightarrow \bullet OH + OH^- + Fe^{3+} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}HOO^{2+} + H^+ \quad (2)$$

$$Fe\text{-}HOO^{2+} + H^+ \rightarrow Fe^{2+} + HO_2\bullet \quad (3)$$

$$\bullet OH + \text{organics} \rightarrow \text{products} \quad (4)$$

*Corresponding author
Email: mmclu@mail.chna.edu.tw

$$H_2O_2 + \bullet OH \rightarrow H_2O + HO_2\bullet \quad (5)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + \bullet OH \quad (6)$$

$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^- \quad (7)$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad (8)$$

Although Fenton process has been successful in the degradation of the organic contaminants present in wastewater. The production of ferric hydroxide sludge ($Fe(OH)_3$) is consider to be an disadvantage of this process which requires further separation and disposal. One of the alternatives to deal with this problem is the use of fluidized-bed Fenton reactor. The carriers in fluidized-bed Fenton reactor can initiate the iron precipitation and/or crystallization process [8], therefore, the production of sludge was reduced. There are several reactions occurring in fluidized-bed Fenton reactor including: (1) homogeneous chemical oxidation (H_2O_2/Fe^{2+}), (2) heterogeneous chemical oxidation (H_2O_2/iron oxide), (3) fluidized-bed crystallization, and (4) reductive dissolution of iron oxides. This study demonstrates the advantage of fluidized-bed Fenton process compared with traditional Fenton process in treating 2,4-DCP. However, the major objective of this study is to determine the optimum conditions and investigate the effects of each parameter on 2,4-DCP degradation by using Box-Behnken statistical design.

MATERIALS AND METHODS

1. Chemicals

2,4-DCP, ferrous sulfate heptahydrated ($FeSO_4\bullet 7H_2O$), H_2O_2 and all chemical substances used in the experiment were reagent grade obtained from Merck. All the preparations and experiments were conducted at the room temperature. The carriers used in this study were silica dioxide (SiO_2), which has a grain-shape with particle diameter of 0.84-2.00 mm. A 1.35 L fluidized-bed reactor was operated in batch mode with a total reaction time of 2 h in all experiments performed. A fluidized-bed reactor is a cylinder vessel which consists of the outlet, the inlet and a recirculation pump.

2. Analytical Method

The samples taken at selected time intervals were immediately injected into the tubes containing NaOH solution to stop further reaction by increasing pH to 11 [8]. The samples were filtered with 0.20 μm syringe micro-filters to separate precipitated iron from the solutions. After that, the residual 2,4-DCP was analyzed by high performance liquid chromatography (HPLC) with the Spectra System model SN4000 pump through Asahipak ODP-506D column (150 mm × 6 mm × 5 μm) coupled with UV1000 detector at 285 nm. A mixture of 60% acetonitrile in 40 vol% de-ionized water was used as mobile phase. The Fe^{2+} was determined by light absorbance measurement at 510 nm after complexed with 1,10-phenanthroline using a UV-Vis spectrophotometer [9]. Residual H_2O_2 was analyzed by titanium oxalate method. Samples were analyzed for residual H_2O_2, Fe^{2+}, total iron, 2,4-DCP, Total iron concentration were analyzed using a Hitachi Z6100 polarized Zeeman atomic absorption spectrophotometer and chemical oxygen demand (COD) was measured by closed reflux titrimetric method based on the Standard Methods [8].

3. Fluidized-bed Fenton Experiments

At the beginning, the synthetic wastewater containing 2,4-DCP was prepared by using de-ionized water and then adjusted initial pH by 1.0 M of H_2SO_4. After that, a calculated amount of ferrous sulfate was added in the volumetric flask containing the synthetic wastewater. The solution was then added into the reactor followed by the carriers. Then, the re-circulated pump was turned on to suspend the carriers and to mix the solution. Hydrogen peroxide was finally added to the solution and the reaction was simultaneously started.

4. Design of Experiments

Most of studies have only focused on the basic single-factor-at-a-time approach, studying the effect of each experimental parameter on the process performance while keeping all other conditions constants [10]. However, this strategy does not consider cross-effects from the factors and lead to a poor-optimization. To overcome this problem, the use of statistical design experiments has proven to be advantageous, allowing the use of the minimum number of experiments while simultaneously changing several variables. Moreover, statistical design experiments can be used for optimization process in multivariable system.

The Design-Expert software version 7.0 (Stat-Ease, Inc., Minneapolis, USA) was used to design the number of experiments to be performed, calculate the experimental data and evaluate the experimental results. In order to investigate the effects of significant factors and to obtain the optimum condition, in this study, the Box-Behnken statistical design was used.

The optimization procedure involves studying the response of statistically designed combination, estimating the coefficients by fitting experimental data to the response functions and predicting the response of fit model [9].

RESULTS AND DISCUSSION

Four important factors affecting the fluidized –

bed Fenton process; namely, pH, initial Fe^{2+}, H_2O_2 concentration and the amount of carriers were selected as a factor in the Box-Behken statistical design. 2,4-DCP, COD and total iron removal efficiencies were represent by a response function. Table 1 shows the levels of the four factors on the Box-Behken statistical design. The low, center and high levels for each variable are designated as -1, 0 and +1, respectively.

The total number of experiment with four variables and three-level in Box-Behnken design were 29 experimental runs, including five replications at the center point (0,0,0,0,0). The complete 29 runs of experimental data and result are shown in Table 2. Results from the experiment revealed that the maximum removal of 2,4-DCP was > 99% while the minimum removal was 65%. The removal of COD and total iron were between 37 and 62% and 2-43%, respectively.

1. Correlation of Each Parameter on 2,4-DCP Removal Efficiency

The correlation of 2,4-DCP removal efficiency with 4 parameters are shown in Table 3. The best correlation of 2,4-DCP removal efficiency was with H_2O_2

Table 1. The levels of variables in Box-Behnken statistical design

Variables	Symbol	Variable level		
		Low (-1)	Center (0)	High (+1)
pH	A	2	3	4
Fe^{2+} (mM)	B	0.1	0.55	1
H_2O_2 (mM)	C	1	5.5	10
Amount of carriers (g)	D	50	150	250

Table 2. Design of experimental runs for the Box-Behnken statistical design of fluidized-bed Fenton process with 1 mM of 2,4-dichlorophenol (2,4-DCP)

Run number	pH	Fe^{2+} (mM)	H_2O_2 (mM)	Carriers (g)	2,4-DCP removal (%)	COD removal (%)	Total iron removal (%)
1	2	0.1	5.5	150	93	37	12
2	4	0.1	5.5	150	93	37	17
3	2	1	5.5	150	93	52	2
4	4	1	5.5	150	93	48	15
5	3	0.55	1	50	69	48	5
6	3	0.55	10	50	> 99	57	6
7	3	0.55	1	250	79	46	5
8	3	0.55	10	250	> 99	48	14
9	2	0.55	5.5	50	96	43	4
10	4	0.55	5.5	50	98	59	22
11	2	0.55	5.5	250	97	53	7
12	4	0.55	5.5	250	97	40	24
13	3	0.1	1	150	71	37	10
14	3	1	1	150	65	49	10
15	3	0.1	10	150	98	56	17
16	3	1	10	150	98	61	12
17	2	0.55	1	150	85	52	4
18	4	0.55	1	150	68	55	12
19	2	0.55	10	150	> 99	62	6
20	4	0.55	10	150	> 99	53	15
21	3	0.1	5.5	50	98	47	10
22	3	1	5.5	50	93	38	6
23	3	0.1	5.5	250	99	41	43
24	3	1	5.5	250	91	46	10
25	3	0.55	5.5	150	98	52	10
26	3	0.55	5.5	150	98	46	11
27	3	0.55	5.5	150	99	55	8
28	3	0.55	5.5	150	97	47	8
29	3	0.55	5.5	150	97	48	9

Table 3. The values of correlation in the removal efficiencies of 2,4-DCP, COD and total iron

Variable	Correlation		
	2,4-DCP	COD	Total iron
pH	-0.077	-0.086	0.482
Fe^{2+} (mM)	-0.096	-0.300	-0.370
H_2O_2 (mM)	0.817	0.109	0.164
Amount of carriers (g)	0.043	-0.127	0.339

concentration. This means that increasing H_2O_2 concentration would improve the degradation of 2,4-DCP. The amount of carriers shows a slight effect on 2,4-DCP removal with the correlation number 0.043, while both Fe^{2+} concentration and pH show the negative correlation. Thus, H_2O_2 has a significant impact on 2,4-DCP degradation with Fe^{2+}, pH and the amount of carriers less significant parameter.

Although, the initial pH does not have an obvious effect on the degradation of 2,4-DCP in our study, the solution pH is an important parameter for Fenton's reactions which controls the production rate of •OH and the concentration of ferrous ion [11]. The reaction of H_2O_2 with Fe^{2+} is significantly affected in low pH condition, causing the reduction in •OH. On the other hand, at high pH condition, the deactivation of Fe^{2+}causes the reduction of •OH due to the formation of ferric hydroxide precipitates ($Fe(OH)_3$) [11] resulting in lower removal efficiency. According to the previous investigations [12,13], the acidic pH level around 3 is usually optimum for Fenton oxidation.

Figure 1a shows the positive effect of H_2O_2 concentration and the optimum value of the Fe^{2+} for maximum 2,4-DCP degradation. Using 1 mM of H_2O_2 and 0.1 mM of Fe^{2+} as the initial concentration can remove 2,4-DCP 70%. Increasing H_2O_2 concentration to 10 mM can increase 2,4-DCP removal to 98%, whereas increasing Fe^{2+} concentration to a high level (0.55 and 1 mM) at 1 mM of H_2O_2 resulted in decreased removal of 2,4-DCP. This negative effect at high Fe^{2+}concentrations can be explained by the fact that Fe^{2+} concentration competes with the organic matter for •OH as shown in Eq. 6. However, ferrous ion and H_2O_2 also compete with 2,4-DCP for the radical scavenging under certain conditions according to Eqs. 2 and 3. These will increase in the rate of hydroxyl radical scavenging leading to the reduction in treatment efficiency [10].

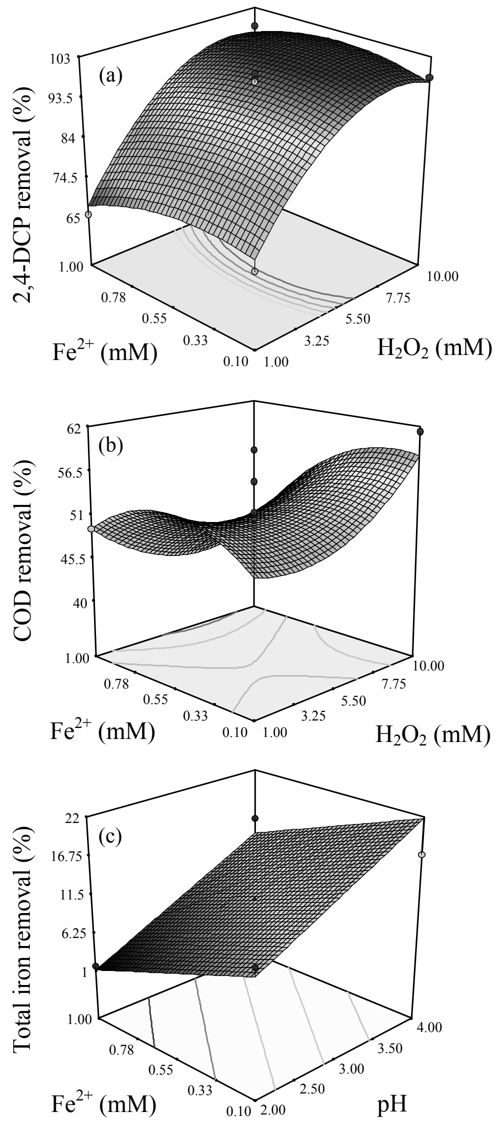

Fig. 1. Three-dimensional representation of the response surface plot of the effect of initial concentration of Fe $^{2+}$ and H_2O_2 on the removal efficiencies of (a) 2,4-DCP, (b) COD and (c) total iron at pH 3, $[Fe^{2+}]$ = 0.55 mM, $[H_2O_2]$ = 5.5 mM and 150 g of carrier.

2. Correlation of Each Parameter on COD Removal Efficiency

The COD removal efficiency depends on the initial concentration of H_2O_2 and of Fe^{2+} with a positive correlation (0.11) with H_2O_2 and negative correlation (-0.30) with Fe^{2+} (Table 3). Or increasing H_2O_2 concentration enhances COD removal, and increasing Fe^{2+} concentration decreases COD removal. pH and the amount of carriers also exhibit a negative effect on COD removal. This means that increasing pH and the amount of carrier resulted in decreased COD removal.

It is seen from Fig. 1b that the maximum COD removal (62%) occurred with the highest H_2O_2 concentration and the lowest concentration of Fe^{2+}. For example, increasing Fe^{2+} more than 0.55 mM could decrease the COD removal efficiency. This was due to the high amount of Fe^{2+} causing scavenging effect of the hydroxyl radicals and hindering the COD degradation.

3. Correlation of Each Parameter on Total Iron Removal Efficiency

The correlation of iron removal with pH, ferrous H_2O_2 concentration and the amount of carriers all yielded a positive effect. This means that iron removal increased when pH, H_2O_2 concentration and the amount of carriers increased. On the other hand, increasing Fe^{2+} concentration could decrease the iron removal. From the correlation number one can summarize that pH value is the main factor affecting the iron removal with the correlation number about 0.48.

As can be seen from Fig. 1c, increasing pH value enhances the total iron removal efficiency. The precipitation of iron hydroxide at high pHs resulted in the decreased dissolve iron. Besides, Fe^{2+} concentration also played an important role in iron removal. Increasing Fe^{2+} concentration would slightly decrease iron removal due to the amount of Fe^{3+} generated from Fenton reaction which could crystallize on the surface of carrier.

The application of Box-Behnken design offers an empirical relationship between the response function and the variables. The equation for the removal of 2,4-DCP by fluidized-bed Fenton process in terms of coded factors are shown below:

$$\begin{aligned}\text{2,4-DCP removal} &= 97.7 - 1.24A - 1.56B + 13.3C + 0.69D - 0.08AB + 4.37AC - 0.32AD \\ &+ 1.36BC - 0.69BD - 2.48CD - 0.57A^2 \\ &- 3.73B^2 - 10.3C^2 + 0.09D^2 \end{aligned} \quad (9)$$

where A, B,C and D are pH, initial Fe^{2+} concentration, initial H_2O_2 concentration and the amount of carriers, respectively.

4. Optimization Process

The main objective of this optimization process was to determine the optimum conditions for removal of 2,4-DCP, COD and iron in fluidized-bed Fenton process by predicting from the experimental data. The optimization module in Design-Expert searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses [14]. The optimum condition for the removal of 2,4-DCP by fluidized-bed Fenton process is pH 3, 100 g of carriers, 0.25 mM of Fe^{2+} concentration and 10 mM of H_2O_2. Therefore, the removal efficiencies of 2,4-DCP, COD and total iron were predicted to be > 99, 61 and 14%, respectively. The actual removal efficiencies when followed these predicted optimum condition were 99% for 2,4-DCP, 55% for COD and 16% for iron. It can be summarized that the experimental results obtained under optimized concentration were close to the predicted results in terms of 2,4-DCP, COD removal and iron removal, evidencing the reliability of the methodology used within the range of concentration investigated.

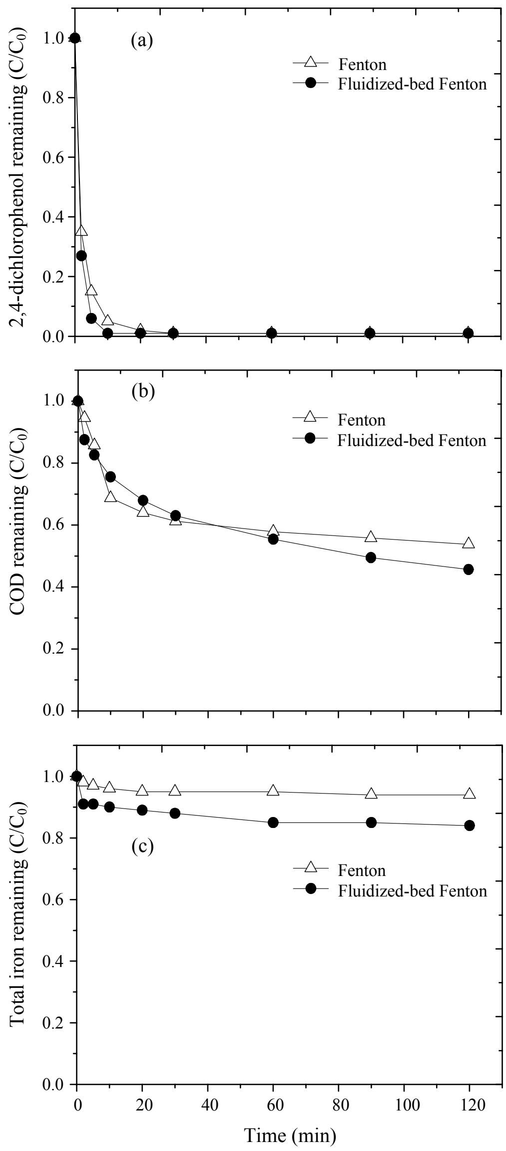

Fig. 2. Comparison of (a) 2,4-DCP, (b) COD and (c) total iron remaining between Fenton and Fluidized-bed Fenton Process with the condition of [2,4-DCP] = 1 mM, [Fe^{2+}] = 0.25 mM, [H_2O_2] = 10 mM, pH = 3 and 100 g of SiO_2.

5. Comparison between the Fluidized-bed Fenton and Fenton Process at the Optimum Condition

The optimum condition obtained from the Box-Benhnken experiment, in the previous part was pH 3, 1 mM of 2,4-DCP, 0.25 mM of Fe^{2+} concentration, 10 mM of H_2O_2 and 100 g of SiO_2.

It can be seen from Fig. 2a that the removal efficiency of 2,4-DCP in fluidized-bed Fenton and Fenton process was almost the same. In terms of COD removal as shown in Fig. 2b, the COD removal efficiency from Fenton and fluidized-bed Fenton process were 45 and 51%, respectively.

The iron remaining in the solution from fluidized-bed Fenton and Fenton process is illustrated in Fig. 2c. There was 6% of iron removal from Fenton process while 16% of iron could be removed in fluidized-bed Fenton process. It can be explained that 16% of iron removal was crystallized on the surface of carrier and 6% of iron left on the dead end of fluidized-bed reactor.

Total irons being removed in fluidized-bed Fenton process can reduce 16% of the amount of sludge occurring after pH adjustment before treatment. Therefore, decreasing in the amount of sludge was considered as an advantage of fluidized-bed Fenton process which also reduces the separation and disposal costs as well.

CONCLUSIONS

The fluidized-bed Fenton process was found to be an efficient method for treating synthetic wastewater containing 2,4-DCP. Box-Behnken design was proven to yield an optimum condition in the removal of 2,4-DCP, including the prediction of the interaction between process variables. Results revealed that under the studied conditions, H_2O_2 concentration was found to be a significant factor affecting 2,4-DCP removal, while the other factors had less effect on 2,4-DCP removal. Increasing H_2O_2 concentration could increase COD removal whereas increasing Fe^{2+} concentration more than 0.55 mM decreased COD removal. Higher concentration of Fe^{2+} adversely affected the COD removal due to the hydroxyl radical scavenging. pH and Fe^{2+} concentration also played an important role in terms of iron removal. The optimum condition for remove 1 mM of 2,4-DCP were pH 3, 100 g of SiO_2, 0.25 mM of Fe^{2+} and 10 mM of H_2O_2 with removal efficiencies of 2,4-DCP, COD and iron > 99, 61 and 14%, respectively. In addition, the optimum condition compared with fluidized-bed Fenton and traditional Fenton process demonstrates the advantage of fluidized-bed Fenton. This process is superior in terms of iron removal by reducing the iron sludge via crystallization process.

ACKNOWLEDGMENT

This research was supported by the Ministry of Education, Taiwan (Grant: P9823), and the National Science Council, Taiwan (Grant: NSC 96-2628-E-641-001-MY3).

REFERENCES

1. Li, X.Z., B.X. Zhao and P. Wang, Degradation of 2,4-dichlorophenol in aqueous solution by hybrid oxidation process. J. Hazard. Mater., 147(1-2), 281-287 (2007).
2. Song, Q., T. Niu and H. Wang, Theoretical study of the reaction of 2,4-dichlorophenol with O_2. J. Mol. Struc.-Theochem., 861(1-3), 27-32 (2008).
3. Zhao, B.X., X.Z. Li and P. Wang, Degradation of 2,4-dichlorophenol with a novel TiO_2/Ti-Fe-graphite felt photoelectrocatalytic oxidation process. J. Environ. Sci., 19(8), 1020-1024 (2007).
4. Glaze, W.H., J.W. Kang and R.H. Chapin, The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Ozone Sci. Eng., 9(4), 335-352 (1987).
5. Esplugas, S., J. Gimenez, S. Contreras, E. Pascual and M. Rodriguez, Comparison of different advanced oxidation processes for phenol degradation. Water Res., 36(4), 1034-1042 (2002).
6. Lu, M.C., J.N. Chen and C.P. Chang, Oxidation of dichlorvos with hydrogen peroxide using ferrous ions as catalyst. J. Hazard. Mater., 65(3), 277-288 (1999).
7. Chou, S., C.C. Liao, S.H. Perng and S.H. Chang, Factors influencing the preparation of supported iron oxide in fluidized-bed crystallization. Chemosphere, 54(7), 859-866 (2004).
8. APHA, Standard Methods for the Examination of Water and Wastewater. 18th Ed., American Public Health Association, Washington, DC (1992).
9. Ay, F., E.C. Catalkaya and F. Kargi, A statistical experiment design approach for advanced oxidation of Direct Red azo-dye by photo-Fenton treatment. J. Hazard. Mater., 162(1), 230-236 (2009).
10. Oliveira, R., F.M. Almedia, L. Santos and M.L. Madeira, Experimental design of 2,4-dichlorophenol oxidation by Fenton's reaction. Ind. Eng. Chem. Res., 45(4), 1266-1276 (2006).
11. Sun, J.H., S.P. Sun, M.H. Fan, H.Q. Guo, Y.F. Lee and R.X. Sun, Oxidative decomposition of *p*-nitroaniline in water by solar photo-Fenton advanced oxidation process. J. Hazard. Mater., 153(1-2), 187-193 (2008).
12. Neyens, E. and J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique. J. Hazard. Mater., 98(1-3), 33-50 (2003).
13. Gallard, H., L.J. De and B. Legube, Effect of pH on the oxidation rate of organic compounds by Fe(II)/H_2O_2. Mechanism and simulation. New J. Chem., 22, 263-268 (1998). (In *French*)
14. Arslan-Alaton, I., G. Tureli and T. Olmez-Hanci, Treatment of azo dye production wastewaters using Photo-Fenton-like advanced oxidation

processes: Optimization by response surface methodology. J. Photochem. Photobio. A-Chem., 202(2-3), 142-153 (2009).

Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-Chief within six months of publication.

Manuscript Received: November 5, 2009
Revision Received: February 13, 2010
and Accepted: February 21, 2010